Structure, optical and photoluminescent properties of hybrid polymer nanocomposites on the base PP+CdS/ZnS

Flora Vidadi Hajiyeva 1,*, Mahammadali Ahmad Ramazanov 2, Habiba Aslan Shirinova 1

1 Baku State University, Azerbaijan, Department Chemical Physics of Nanomaterials, AZ 1148, Zahid Khalilov Str. 23, Baku, Azerbaijan
2 Baku State University, Azerbaijan, Department Chemical Physics of Nanomaterials, Nanoresearch Laboratory, AZ 1148, Zahid Khalilov Str. 23, Baku, Azerbaijan

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* Corresponding Author Email: flora_1985@mail.ru

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Abstract
In this work, PP+CdS/ZnS transparent hybrid polymer nanocomposites were synthesized and studied. The nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive (EDS), and UV-spectroscopy analysis. It was found that the bandgap of PP+1%CdS/ZnS, PP+3%CdS/ZnS, and PP+5%CdS/ZnS nanocomposites is 5.2 eV, 5.1 eV, 4.6 eV, respectively. SEM analysis showed that the ZnS and CdS nanoparticles are evenly distributed in the polymer matrix. Furthermore, the average size of nanoparticles in the PP+3%CdS/ZnS, PP+5%CdS/ZnS nanocomposites are 40-54 nm, 29-56 nm, respectively. Photoluminescence properties of hybrid PP+CdS/ZnS nanocomposites were also investigated. It was established that introduction of ZnS and CdS semiconductor nanoparticles into the polypropylene matrix leads to expanding the region of the spectral sensitivity of hybrid nanocomposites. The photosensitivity of PP+CdS/ZnS nanocomposite films was also investigated.

Keywords: Cadmium Sulfide; Nanocomposite; Nanoparticles; Photoluminescence; Polymer; Polypropylene; Zinc Sulfide.

INTRODUCTION
Today one of the most attractive materials in the field of material science is hybrid nanocomposites. This is primarily because these nanocomposites combine the properties of individual components that make up their composition. It is known that nanoparticles differ in their properties from bulk materials as well as from the individual atoms that make them up. Nanoparticles are characterized by small size, complex internal organization, the ability to pack very tightly, and a very high surface area to volume ratio. Surface atoms make a large contribution to the thermodynamic characteristics of a solid and, for nanoparticles, largely determine the structural and phase transitions. Since very large energy accumulates in the surface of nanoparticles, their stabilization is important, as much as their synthesis. Since very large energy accumulates in the surface of nanoparticles, their stabilization is important, as much as their synthesis. From this perspective, polymers are very effective materials for stabilization nanoparticles. Nowadays, one of the promising directions in polymer science and materials science is the development of scientific principles of production of a new class of materials - polymer nanocomposites. The unique properties of polymer nanocomposites are related not only to the extremely small sizes of metallic or semiconductor filler but also to the structural features of the polymer matrix. The role of the polymer matrix is to allow nanoparticles to be organized into supramolecular structures, which significantly enhances the unique properties of nanoparticles. The opportunity to
manipulate the size and shape of semiconductor nanocrystals (quantum dots) provides a high degree of control over their optical and electronic properties. This control can be used for applications in biological assays, in electronic integral, and the development of wireless systems. It is possible that control the absorption spectrum for photovoltaic, photoluminescent, stimulated emission, and electroluminescent applications due to resizing of quantum dots. Furthermore, as in biological applications size-control of nanoparticles allows spectral multiplexing and coding [1].

Semiconductor (for example, elements of AII BVI and AIV BVI group) based nanocomposites possess unique optical properties. They are promising materials as active elements of nonlinear optics and nanoelectronic devices [2-7]. It is also known that optical characteristics of nanosystem depend not only on the nature of the components but also on the size of nanoparticles and their concentration. In some cases, the description of the properties of a nanocomposite material can be carried out in the framework of the continuous medium approximation. The optical properties of glasses, colored with metals are explained by the approximation of the monodisperse, spherically-symmetric particles that are distributed in a glass matrix uniformly. In this case, assume that the particle size is much less than the average distance between particles, which, in turn, is much less than the wavelength of visible light. This approach explains many of the optical features glass systems. At the same time, it should be also noted that the size of semiconductor nanoparticles affects their band structure. The effect of particle size on the band structure of a solid was studied to explain the optical properties of semiconductors. It is known that atomic orbitals of individual atoms that nanoparticles consist on form generalized molecular orbitals. These molecular orbitals are delocalized into a band structure. This delocalization is characteristic for solid state. In this case, delocalization always begins from the zone-center, and for small particle size, only the zone-centers have a continuous electron density, while zone-edges consist of discrete levels. Thus, a decrease in the size of metal particles (the Fermi level of which lies in the center of the band) down to 3-5 nm at temperatures above several degrees Kelvin does not lead to a change in their electrical and optical properties in comparison with bulk metals. On the other hand, the Fermi level lies between the occupied valence and the unoccupied conduction bands in semiconductors, and it is the band edges that determine the optical and electrical properties. Thus, the optical transitions between the bands strongly depend on the size of the semiconductor particles up to 20-30 nm, after which the bands have a completely continuous energy spectrum.

This paper aims to develop and study hybrid polymer nanocomposites based on polypropylene (PP) polymer, CdS, and ZnS nanoparticles. As known, PP is a high-volume commodity polymer and offers key features including excellent chemical and fatigue resistance and good environmental stress cracking resistance, also high mechanical properties, ease of machining, along with excellent process ability by extrusion, and injection molding. When compared with its competitive thermoplastics, the major advantages of PP can be expressed in terms of specific modulus, heat deflection temperature, and Young’s modulus to cost ratio [8]. Taking into account the elasticity, optical transparency, easy process ability, and good operational properties of PP, it can be assumed that the use of this polymer as a matrix can affect the complex electrophysical, operational (strength, durability, etc.), and active (photoluminescent, photovoltaic, etc.) properties of nanocomposites based on it. It is considered that the study of such ternary polymer nanocomposites will lead to the development of new, highly efficient, multifunctional, hybrid polymer nanocomposites with distinctive physical and chemical properties.

**EXPERIMENTAL SECTION**

**Materials**

All chemicals were used as received without purification: polypropylene (PP grade Moplen HF500N, homopolymer); density 0.92g/cm³ at 25°C, Mₘ=250000, Mₙ= 67000, melting T=162°C), cadmium chloride (CdCl₂·5H₂O, Sigma Aldrich C3141), sodium sulfide (Na₂S·9H₂O, PLC 141687), CTAB (cetyltrimethylammonium bromide, C₁₉H₄₂BrN, AB 117004, 98% chemically pure), zinc chloride (ZnCl₂, PLC 141779 - for analysis, anhydrous), toluene (PLC 141745).

**Preparation of CdS, ZnS NPs and PP+CdS/ZnS based nanocomposites**

CdS and ZnS NPs were prepared by the chemical co-precipitation method. Nanoparticles were synthesized in the presence of cationic
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surface-active substance CTAB as follows: 0.05 M CdCl₂ solution was mixed with 0.5% CTAB solution in a magnetic stirrer for 10 minutes. Further, the solution of 0.05 M sodium sulfide (Na₂S) was added to the primary solution and was stirred intensely at ambient temperature for two hours. To remove non-interacting ions Cd²⁺ and S²⁻ and get purified CdS NPs, the mixture several times distilled with deionized water and ultracentrifuged for 10 minutes. The colloidal nanoparticles solution was treated with ultrasound by VSX 500 ultrasonicator, to break down the formed agglomerates and aggregates. Purified CdS NPs were transferred into the Petri dish and were dried for 24 hours [9]. ZnS nanoparticles were prepared by the same method. To synthesis ZnS nanoparticles, 0.05 M ZnCl₂ and 0.05 M Na₂S solutions were taken as precursors. For the synthesis of PP+CdS/ZnS nanocomposites, 0.1 g PP powder was dissolved in the toluene solvent. CdS and ZnS NPs in different weight contents (1%, 3%, 5%, 10%) were added into PP solution and mixed on a magnetic stirrer for 4 hours almost at 80°C. Then the homogeneous mixture was transferred to the Petri dish and put to dry for a day. For completely removing the solvent from the volume of the polymer, the nanocomposite samples were dried in a vacuum oven for 1 hour. Thin nanocomposite films were obtained by a hot pressing method at the melting temperature of PP (170°C) and a pressure of 10 MPa. The cooling of the nanocomposite films after hot pressing was carried out in the water at a cooling rate of 200 deg/min.

characterization
x-ray diffraction analysis was performed on a Rigaku Mini Flex 600 XRD diffractometer, equipped with Cu K-α radiation at room temperature. Scanning electron microscopy was used to investigate the morphology of the nanocomposite samples (SEM, Jeol, JSM-7600 F). Scanning was performed in LEI mode, at an accelerating voltage of 15 kV, and a working distance of 4.5 mm. Energy dispersive micro-X-ray analysis was performed by using the device X-Max 50 (Oxford Instruments). The UV spectra have been recorded on Spectrophotometer Specord 250 Plus at 200-700 nm at ambient temperature. Photoluminescence properties of nanocomposite films were examined using a spectrofluorimeter Varian Cary Eclipse at wavelength range 200-900 nm. For studying the properties of photoconductivity, we used an M833 automated double dispersion monochromator (spectral resolution ~ 0.024 nm at a wavelength of 600 nm) with computer control and a detector that records radiation in the wavelength range of 350–2000 nm. The photoconductivity spectra of samples, with dimensions of 0.6×2×6 mm³, were recorded in the modes of constant or intensity-modulated radiation at a frequency of 4.8 kHz. The photocurrent and laser radiation pulses were recorded using a technique that allows recording single nanosecond pulses on the screen of a storage oscilloscope (Tektronix TDS1002B).

results and discussion

xrd analysis
fig. 1a shows the diffraction patterns of CdS nanoparticles. It was found that the main peaks at 24.9° (002); 26.6° (101); 28.3° (102); 36.8° (110); 43.9° (103); 48.1° (200); 51.10° (112); 52.1° (201); 53.1° (004); 54.9° (202); 67.1° (203); 69.6° (210); 71.2° (211); 72.8° (114), 75.9° (105) of 2q angle belonging to the crystalline planes of the CdS hexagonal structure. The crystal lattice parameters are 4.16°, 4.16° and 6.77 A° according to the Card ICCD PDF database (00-101-1054)[10-20]. Fig. 1b shows the diffraction patterns of ZnS nanoparticles. It was found that the main peaks in the diffractogram at 2q values of 28.5° (002), 30.5° (101), 39.5° (102), 47.5° (110), 51.5° (103), 56.5° (112), and 73.0° (203) belong to zinc sulfide nanoparticles with a hexagonal crystal lattice of the wurtzite type, according to the ICCD PDF database (00-101-1195) [20-23]. Other peaks observed in the diffractograms of CdS and ZnS, belong to the CTABr stabilizer.

fig. 2 shows the diffraction patterns of PP nanocomposites. It was found that the main peaks in the diffractogram at 2q values of 28.5° (002), 30.5° (101), 39.5° (102), 47.5° (110), 51.5° (103), 56.5° (112), and 73.0° (203) belong to zinc sulfide nanoparticles with a hexagonal crystal lattice of the wurtzite type, according to the ICCD PDF database (00-101-1195) [20-23]. Other peaks observed in the diffractograms of CdS and ZnS, belong to the CTABr stabilizer.

Fig. 2 shows the diffraction patterns of PP (a) and hybrid polymer nanocomposites based on PP+CdS/ZnS (b) depending on the content of CdS and ZnS nanoparticles. The XRD pattern of PP shows five major peaks at the 5–30° range of 2q. However, any peaks corresponding to the beta (β) and gamma (γ) form of PP crystals do not observe. This fact confirms the presence of only the monoclinic α-form of PP crystal (Fig 2a). As can be seen from Fig. 2b, with the introduction of CdS and ZnS nanoparticles into the PP matrix, the intensity of peaks at 13.71°; 16.54°, and 18.2°, corresponding to the crystalline phase of polypropylene, decreases. With the introduction of 1% CdS, and ZnS nanoparticles into the PP matrix the peak intensity at 2q=21.43° increases. The small peaks at 2q values of 24.9° (002), 26.6°...
Fig. 1. Diffraction patterns of CdS (a) and ZnS (b) nanoparticles.

Fig. 2. Diffraction patterns of PP (a) and PP+CdS/ZnS (b) nanocomposites depending on the content of CdS and ZnS nanoparticles: 1. PP+1%CdS/ZnS; 2. PP+5%CdS/ZnS; 3. PP+10%CdS/ZnS.
(101), 28.3° (102), that belong to cadmium sulfide nanoparticles, and maximums at 39.5° (102) and 56.5° (112) that correspond to zinc sulfide nanoparticles were observed at the diffractogram of the PP+10% CdS/ZnS based nanocomposite.

**UV-analysis**

The width of the forbidden band was calculated for polymer nanocomposites through extrapolation of the UV absorption spectrum. Following equation was used for calculation:

\[
\alpha = A \left( h\nu - E_g \right)^n / h\nu
\]

Where A-constant, n-1/2 for allowed direct transition, \( h\nu \)- photon energy, \( E_g \)- width of the forbidden band.

Fig. 3a shows the absorption spectra and the optical absorption edge for nanocomposites based on PP+ZnS, PP+CdS, and PP+CdS/ZnS. Fig. 3b reports the plot of \( (\alpha h\nu)^2 \) versus the energy of the nanocomposite. By extrapolating the linear portion near the onset of absorption edge to the energy axis the band gap energy of nanocomposite samples can be determined. It was found that for PP+ZnS, PP+CdS, and PP+CdS/ZnS nanocomposites the band gap is 3.65 eV, 2.8 eV, and 4.25 eV, respectively [14-21].

Fig. 4a shows the absorption spectra of PP+CdS/ZnS nanocomposites depending on the concentration of ZnS and CdS nanoparticles. Fig. 4b shows the optical absorption edge for PP+CdS/ZnS nanocomposites. It was found that the band gap of PP+CdS/ZnS nanocomposites decreases with an increase in the content of ZnS and CdS nanoparticles. Furthermore, It was determined that the band gap of PP+1%CdS/ZnS; PP+3%CdS/ZnS, and PP+5%CdS/ZnS; PP+10%CdS/ZnS nanocomposites are 5.2 eV; 5.1 eV; 4.6 eV, respectively. The decrease in the band gap of the hybrid nanocomposites depending on filler content was explained by the fact that depending on the concentration of ZnS and CdS nanoparticles their size increase and agglomeration occurs [22-23].

Furthermore, the absorption band in the wavelength range of 270-300 nm belongs to CdS nanoparticles. The low-intensity absorption edge in the region of 400 nm belongs to ZnS nanoparticles. The appearance of this peak with an increase in the filler concentration in PP+CdS/ZnS nanocomposites indicates that the nanoparticles are covered with a thin layer of ZnS.

**SEM analysis**

Fig. 5 shows SEM images of PP+3%CdS/ZnS (Fig. 5a) and PP+5%CdS/ZnS (Fig. 5b) hybrid nanocomposites. SEM images show that ZnS and CdS nanoparticles are evenly distributed within the polymer matrix.

It was found that with an increase in the concentration of nanoparticles, the average
size of both zinc sulfide and cadmium sulfide nanoparticles increases. The average nanoparticle size in PP+3%CdS/ZnS (Fig. 5a) and PP+5%CdS/ZnS nanocomposites are 40-54 nm (Fig. 5b) and 29-56 nm, respectively. The energy-dispersive spectrum (EDS) of PP+CdS/ZnS hybrid nanocomposite was shown in Fig. 6. According to the EDS spectrum, the polymer nanocomposite consists of individual CdS, ZnS nanoparticles, and polypropylene polymer. However, the signal of the Al element comes from the aluminum substrate used during SEM analysis.

Photoluminescence study.

Fig. 7 shows the photoluminescence (PL) spectra of PP+CdS, PP+ZnS, and PP+CdS/ZnS nanocomposites. The excitation wavelength for study PL spectra of the PP+CdS nanocomposite was 398 nm (Fig. 7a). The wavelength of light for the investigation of the PL spectra of the PP+ZnS nanocomposite was 260 nm (Fig. 7b). The PP+CdS/ZnS nanocomposite was excited by light with a wavelength of 260 nm (Fig. 7c).

As can be seen from the Fig. 7 a, the peaks at 446 nm (2.78 eV), 458 nm (2.71 eV), 465 nm (2.67 eV)
eV), 517 nm (2.40 eV), 528 nm (2.35 eV), 542 nm (2.29 eV), 567 nm (2.19 eV) and 573 nm (2.16 eV) belong to CdS nanoparticles [24-28]. For single-crystal CdS, the emission wavelength during the inter-band recombination is 517 nm. A blue shift-reduction of the emission wavelength is observed for CdS quantum dots. Other peaks observed in the PL spectrum of PP+CdS/ZnS nanocomposites are due to energy dissipation. According to the PL spectra data, it can be concluded that upon preparation of hybrid nanocomposites, such as PP+CdS/ZnS, the spectrally sensitive region of the spectrum also broadens.

The photoluminescent properties of PP+CdS/ZnS hybrid nanocomposites are investigated
depending on the concentration of CdS and ZnS nanoparticles. Figs. 8, 9, and 10 show the PL spectra of PP+CdS/ZnS nanocomposites that obtained by various excitation wavelengths. A change in the excitation wavelength leads to a relative change in the intensity of the fluorescence peaks at the 430–530 nm regions. With an increase in the excitation wavelength, the intensity of the short-wavelength peaks, especially the peak at 430 nm, decreases, while the emission above 530 nm does not change. Thus, a change in the excitation energy leads to a change in the radiation intensity associated with the relaxation of free electrons, migration, the capture of excitons by shallow traps, and their recombination. In this case, the intensity of recombinations via deep levels does not change [29-37].

Fig. 11 shows the excitation and emission
Fig. 11. Excitation and emission spectra of the PP+CdS/ZnS nanocomposites.
spectra of the PP+CdS/ZnS nanocomposite. It can be seen that the excitation and emission spectra are mirror reflections of each other, which proves that the peaks in the PL spectra at wavelengths of 406 nm (Fig.11a), 456 nm (Fig.11b), 486 nm (Fig.11c), 512 nm (Fig.11d), 530 nm (Fig.11e), 540 nm (Fig.11f), 560 nm (Fig.11g), 576 nm (Fig.11h), and 647 nm (Fig.11i) are luminescent, belonging to PP+CdS/ZnS hybrid nanocomposites.

There are two isolated bands in the PL spectra of PP+CdS/ZnS nanocomposites. The maximums at 530 nm and 650 nm are observed during excitation by light with 375 nm and 475 nm wavelength, respectively. No bands with a maximum at 650 nm are observed in the luminescence spectra of the sample with CdS nanoparticles. It can be assumed again that the appearance of a band with a maximum at 650 nm is due to the coating of CdS nanoparticles with a ZnS shell (Fig. 12).

Photosensitivity of nanocomposites

Fig. 13 shows the curve of the spectral distribution of the photocurrent for a nanocomposite based on PP+10%CdS/ZnS with different contents of CdS and ZnS nanoparticles depending on the wavelength. As can be seen from Fig.13, the nanocomposite exhibits photosensitivity in the wavelength range of 310-590 nm. It was found that in the short and long wavelength parts of the spectrum, maxima are observed at 350 nm and 500 nm, corresponding to the band gap of ZnS (E_g = 1.24/0.350 = 3.54 eV) and CdS (E_g = 1.24/0.500 = 2.48 eV) nanoparticles, respectively. The presence of both maxima indicates that the CdS and ZnS nanoparticles don’t form a solid solution in the PP matrix.

Consequently, found that the thin films based on PP+CdS/ZnS are highly efficient materials with good optical, photoluminescent, and...
photoresistive properties, which directly makes it possible to use these materials as elastic thin-film solar cells, converters, sensors, displays, elastic photoresistors, etc.

CONCLUSION

PP+CdS/ZnS hybrid polymer nanocomposites were synthesized and studied. Polymer nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive (EDS), and UV-spectroscopy analysis. It was found that the band gap of PP+1% CdS/ZnS, PP+3% CdS/ZnS, and PP+5% CdS/ZnS, PP+10% CdS/ZnS hybrid nanocomposites is 5.2 eV, 5.1 eV, 4.6 eV, respectively. SEM analysis showed that the ZnS and CdS nanoparticles are evenly distributed in the polymer matrix. The average size of nanoparticles in the PP+3% CdS/ZnS, PP+5% CdS/ZnS nanocomposite is 40-54 nm, 29-56 nm, respectively. Photoluminescence properties of PP+CdS/ZnS hybrid nanocomposites were also investigated. It was established that the introduction of ZnS and CdS semiconductor nanoparticles into the polypropylene matrix, leads to expanding the region of the spectral sensitivity of hybrid nanocomposites. The photosensitivity of PP+CdS/ZnS nanocomposite films was also discovered.

CONFLICT OF INTEREST

Authors have no conflict of interest.

REFERENCES


